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(54) HOT DIP GALVANNEALED STEEL SHEET AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the image clarity of a steel sheet after coating and the flaking resistance of plating coating by forming Al-contg. Fe-Zn alloy plating film having specified surface roughness on a dead-soft steel having a specified compsn.

SOLUTION: The compsn. of a steel is, by weight, ≤0.004% C, 0.03 to 0.13% Si, 0.05 to 0.4% Mn, 0.007 to 0.02% P, 0.018 to 0.05% Ti, 0 to 0.02% Nb, 0.005 to 0.1% Al, 0 to 0.005% B, and the balance Fe with inevitable impurities. On at least one side of a steel sheet produced from the steel having this compsn., Fe-Zn alloy plating film contg. 0.18 to 0.5% Al is formed. The surface roughness of this plating film is regulated to ≤1μm by arithmetic average roughness (Ra), and the number of the peaks of troughs is regulated to 320 to 600/25.4mm. Furthermore, it is preferable that the steel sheet before the plating is retained in the temp. range of 600 to 500°C for 20 to 60sec in a reducing atmosphere composed of hydrogen and nitrogen and in which the dew point is regulated to -20 to -40°C.

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(0013) steel (0044)
(0091) FeZn

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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] They are below C:0.004 % and Si at weight %. : 0.03 - 0.13%, Mn :0.05-0.4 %, P:0.007 - 0.02%, Ti : 0.018 - 0.05%, Nb : 0 - 0.02%, aluminum : 0.005 - 0.1%, B:0 - 0.005%, The remainder is Fe. Steel which consists of an unescapable impurity is used as a base material. At least and on the one side aluminum It contains below 0.18%or more 0.5 %, and the surface roughness is 1 micrometer at arithmetic mean granularity (Ra). Following, The number of trough peaks: Fe-Zn which is 320-600 / 25.4mm Alloying hot-dip zinc-coated carbon steel sheet excellent in the paint image clarity and flaking-proof nature which are characterized by having an alloy-plating coat.
[Claim 2] The process which make a base material pile up in the temperature requirement of 600 - 500 ** 60 or less seconds 20 seconds or more in the process heat before galvanize a base material in the reducing atmosphere which a dew-point become from the hydrogen which be the range which be -20--40 degree C, and nitrogen be include, and it be 0.11 % of the weight or more 0.14 or less % of the weight of aluminum. The manufacture approach of the alloying hot-dip zinc-coated carbon steel sheet according to claim 1 characterize by to perform alloying processing after galvanize using the plating bath to contain.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the alloying hot-dip zinc-coated carbon steel sheet which is excellent in the plating-proof detachability at the time of processing, and the image clarity after paint and which is used mainly for automobiles, and its manufacture approach.
[0002]
[Description of the Prior Art] In recent years, in household electric appliances, building materials, and the industrial field of an automobile, the hot-dip zinc-coated carbon steel sheet is used in large quantities. The alloying hot-dip zinc-coated carbon steel sheet is especially widely used in respect of economical efficiency, a rust-proofing function, and the engine performance after paint.
[0003] Usually, a hot-dip zinc-coated carbon steel sheet performs suitable cleaning washing for a base material, anneals it by the reducing atmosphere which consists of hydrogen and nitrogen, and is manufactured by cooling to near plating temperature and being immersed in a melting zinc bath. An alloying hot-dip zinc-coated carbon steel sheet heats the steel plate which carried out hot dip zincing for 3 - 60 seconds by 500 - 600 **, and is Fe of a base material. A galvanization layer is diffused and it is Fe-Zn. An alloy layer is made to form and it manufactures. Generally, it is Fe of an average of a plating layer. A content is 8 - 12 % of the weight, and plating coating weight is per [20] one side - 70 g/m2. Since manufacturing in the usual means is difficult for that in which coating weight is less than this range and the thing exceeding this range is difficult to secure the powdering-proof nature of a plating layer, generally it is not supplied.
[0004] Thus, the manufactured alloying hot-dip zinc-coated carbon steel sheet performs press working of sheet metal, is processed into a predetermined configuration and painted. In order to prevent the low-temperature chipping which is easy to produce at the time of the use after powdering which is easy to produce at the time of press working of sheet metal, a flaking, and paint, the adhesion of a plating coat is required of this alloying hot-dip zinc-coated carbon steel sheet.
[0005] Moreover, importance is attached also to the result appearance of the painted product being good, and the steel plate with the sufficient image clarity after the paint it is [paint] the index is also called for.
[0006] Powdering is the phenomenon in which a plating coat becomes powder and exfoliates in the field in which a steel plate receives a compression set at the time of press working of sheet metal. Zn which the corrosion resistance of the part deteriorated and was generated when powdering arose Powder adheres to metal mold and spoils the appearance quality of mold goods. It is Fe-Zn at the process of alloying. An alloy progresses too much and it is hard Fe-Zn of ** equality. If an alloy layer arises superfluously, it is said that powdering becomes remarkable. Powdering managed whenever [plating coating weight and alloying] etc., and the improvement has been achieved.
[0007] A low-temperature chipping is the phenomenon in which a plating coat exfoliates with a paint film from an interface with a base material, when a pebble collides with the car body of an automobile in a low-temperature region 0 degree C or less at high speed. This is the problem of the adhesion on a

plating coat and the front face of a base material, and in order to improve low-temperature chipping nature, the method of adjusting the granularity on the front face of a base material which touches a plating coat etc. is proposed.
[0008] In the case of press working of sheet metal, a steel plate slides on the front face of metal mold. At this time, a part of plating coat may become a thin film integrated circuit, and it may exfoliate. This phenomenon is called the flaking. If a flaking arises, it will change the blank holder pressure at the time of press working of sheet metal, and it not only spoils the appearance quality of mold goods, and corrosion resistance, but will become causes, such as press fracture and a defect of shape. Although the cause which a flaking generates is in the brittleness of a plating coat, or the poor adhesion between a plating coat and a base material front face, what is influenced most greatly is the frictional resistance between a steel plate and the metal mold which checks the inflow of a steel plate.
[0009] Although it is possible to make surface roughness of a plating coat coarse and to raise the holdout of the lubricant at the time of press working of sheet metal as an approach of preventing a flaking, it is a problem that the image clarity after the paint this approach of whose the surface roughness of a plating coat becomes coarse and is quality important as a sheathing application of an automobile is spoiled.
[0010] As a remedy to a flaking, it is Fe on an alloying hot-dip-zincing coat as indicated by for example, the publication-number No. 236984 [05 to] official report. There is a method of electroplating a thin film and improving the skid nature of a plating steel plate. However, by this approach, since electroplating must be further given on a hot-dipping steel plate, economical efficiency is spoiled.
[0011]
[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is offering the alloying hot-dip zinc-coated carbon steel sheet excellent in the image clarity after paint, and the flaking-proof nature of a plating coat, and its manufacture approach about the alloying hot-dip zinc-coated carbon steel sheet used mainly for an automobile.
[0012]
[Means for Solving the Problem] The summary of this invention is in the alloying hot-dip zinc-coated carbon steel sheet excellent in the paint image clarity and flaking-proof nature which were indicated to following (1), and its manufacture approach indicated to (2).
[0013] (1) They are below C:0.004 % and Si at weight %. : 0.03 - 0.13%, Mn :0.05-0.4 %, P:0.007 - 0.02%, Ti : 0.018 - 0.05%, Nb : 0 - 0.02%, aluminum : 0.005 - 0.1%, B:0 - 0.005%, The remainder is Fe. Steel which consists of an unescapable impurity is used as a base material. At least and on the one side aluminum It contains below 0.18%or more 0.5 %, and the surface roughness is 1 micrometer at arithmetic mean granularity (Ra). Following, The number of trough peaks: Fe-Zn which is 320-600 / 25.4mm Alloying hot-dip zinc-coated carbon steel sheet excellent in the paint image clarity and flaking-proof nature which are characterized by having an alloy-plating coat.
[0014] (2) Include the process which makes a base material pile up in the temperature requirement of 600 - 500 ** 60 or less seconds 20 seconds or more in the process heated before galvanizing a base material in the reducing atmosphere which a dew-point becomes from the hydrogen which is the range which is -20--40 degree C, and nitrogen. And 0.11-% of the weight or more 0.14 or less % of the weight of aluminum The manufacture approach of an alloying hot-dip zinc-coated carbon steel sheet given in the above (1) characterized by performing alloying processing after galvanizing using the plating bath to contain.
[0015] this invention person etc. acquired the knowledge of the following related with many properties of a plating coat, and completed this invention.
[0016] ** In the front face of a plating coat, a diameter is [the heights of the shape of a plateau, and the shape of an intermittent bank, and] 2-20 micrometers. There is the minute depression section of order. These heights have many which have been produced centering on the grain boundary on the front face of a base material, and many depression sections in the location which corresponds in the crystal grain on the front face of a base material conversely are accepted. These heights have many from which that crowning is a plane in response to the effect of skin pass rolling performed after alloying, leveler plate

leaping, etc. The crystal grain of an alloy plating is observed by the another side depression section, and it is thought that the front face after an alloying reaction is maintained. Hereafter, the depression section with this minute plating front face is described as a "crater."
[0017] The heights or the crater of a plating coat front face is Fe-Zn between a base material and a plating coat. It is generated when alloying reactivity differs in the crystal grain of a base material in a grain boundary. Since reactivity is high compared with the inside of crystal grain, the direction of the grain boundary is Fe-Zn in a grain boundary. An alloying reaction advances early and the plating coat of the part equivalent to the grain boundary upper part becomes convex. A crater increases relatively in the crystal grain internal phase this section with a slow alloying reaction.
[0018] ** The occurrence frequency of the crater of a plating coat front face has the number of trough peaks (the number of troughs which is measured between 25.4mm of measurement length here and to which the depth of the trough exceeds 50% of the depth of the deepest trough) and correspondence required in cross-section curvilinear measurement of surface roughness. The number of trough peaks becomes large as the number of craters increases, what has the larger number of trough peaks has smaller coefficient of friction, and a flaking cannot generate it easily.
[0019] ** It is Ti to super-low C steel. Nb It adds, C in steel is fixed as a sludge, steel which restricted P and B content further is used as a base material, and it is aluminum. By alloying, after carrying out hot dipping using a galvanization bath with a high content, the increase of the number of craters and the number of trough peaks can be enlarged. This is aluminum of a plating coat. When a content is high, it is surmised that it is because the difference of the alloying reaction rate between the grain boundary on the front face of a base material and the inside of crystal grain is expanded.
[0020] ** When the front face of a plating coat has many craters in this way, generally, surface roughness becomes coarse, and the image clarity after paint deteriorates, and become less desirable for a sheathing application. However, it is Si of optimum dose to a base material. It is made to contain, and if low-temperature maintenance is carried out in a specific reducing atmosphere, the base material which recrystallization ended is galvanized after that and alloying processing is carried out in the heating process before plating, the image clarity after increasing the crater on the front face of plating, and also painting can be made to improve.
[0021] This reason is presumed as follows. Fe-Zn Alloying reactivity is influenced of the crystal texture of a base material. For this reason, the crystal with the high reactivity of alloying and the low crystal exist in the base material front face according to the difference of that texture. Since there are few reactant differences between a grain boundary and the inside of a grain, it is hard to produce a crater as a crystal with high reactivity, for example, the crystal of {100} texture which the {100} sides of a crystalline are accumulating on a base material front face and parallel. On the other hand, since the reactant difference between a grain boundary and the inside of a grain is large, a crater is more clearly generated as a crystal with low reactivity, for example, the crystal of {111} texture which the {111} sides of a crystalline are accumulating on a base material front face and parallel.
[0022] Si With the added steel, it is Si to the base material maximum surface section at the time of reduction annealing. An oxide condenses and the alloying reactivity on the front face of a crystal falls. At this time, reactivity falls [the crystal of the texture where reactivity is high] greatly. Si Although it is in the inclination for the reactivity of a grain boundary to also fall by concentration of an oxide, the direction of the reactivity in crystal grain falls more greatly. For this reason, the reactant difference of a grain boundary and the inside of a grain is expanded, and it is Si. Many craters come to be accepted rather than the steel which is not added. Furthermore, in order for the reactivity of the crystal of the texture where reactivity is high to fall greatly especially, the reactant difference during a crystal becomes small, and it is thought that the difference of the depth of a crater contracts and the arithmetic mean granularity on the front face of plating decreases.
[0023]
[Embodiment of the Invention] On the occasion of operation of this invention, the reason which limited each factor and conditions is explained below. In addition, % display described below means weight %.
[0024] (1) Chemical composition C of a steel plate : since the workability of a steel plate is spoiled, few

C contents are so desirable that there are. Moreover, it segregates to the grain boundary of a base material, and C which is dissolving in steel is Fe-Zn in the grain boundary. An alloy reaction is delayed and there is an operation which controls generation of a crater as a result. It is Ti in order to secure the workability of a steel plate, and the number of trough peaks of a plating coat front face in this invention. Nb It is made to contain, and C is fixed and defanged. It is Ti if C content increases. Nb Since it must add so much, in economical efficiency's being missing, carbide increases superfluously and also spoils the workability of a steel plate. For this reason, the upper limit of C content is made into 0.004 %. It is below 0.003 % preferably.

[0025] Si : Si of optimum dose If it is made to contain, when carrying out reduction annealing of the base material, it is Si to a base material front face. The crater of a plating coat front face is made to increase by producing an oxide. The holdout of the lubricant which this uses at the time of processing improves, and a flaking can be prevented. It is effective in decreasing the surface roughness on the front face of a coat to coincidence, and improving the image clarity after paint to it. The minimum is made into 0.03% in order to acquire such effectiveness. Si on the front face of a base material If an oxide becomes superfluous, the difference of alloying reactivity between grain boundaries will decrease in crystal grain, and the number of trough peaks will decrease too much. For this reason, that upper limit is made into 0.13%.

[0026] Mn : in order to inhibit the hot shortness resulting from S mixed into steel as an unescapable impurity, it is made to contain 0.05% or more. If it adds superfluously, since the workability of a steel plate will be spoiled, the upper limit is made into 0.4 %.

[0027] P: It is a suitable element to raise the reinforcement of a steel plate without spoiling workability. In this invention, in order to increase a crater and to secure the number of trough peaks, IF steel (Interstitial Free steel) of super-low C is used. However, since a certain amount of reinforcement as a steel plate for automobile car bodies is required, P is made to contain and reinforcement is held. Therefore, the minimum of P content is made into 0.007 %. If P is added superfluously, it will segregate to the grain boundary of a base material, and the alloying reaction in a grain boundary is controlled, and the number of trough peaks decreases. For this reason, the upper limit of P content is made into 0.02%.

[0028] Ti : the dissolution C of super-low C steel is fixed, and in order to raise the alloying reactivity in the grain boundary, it is made to contain more than 0.018 %. Since economical efficiency will be spoiled if it adds superfluously, the upper limit is made into 0.05%.

[0029] Nb : it is Ti although additive-free is sufficient. Since there are effectiveness which fixes Dissolution C similarly, and effectiveness which makes small the diameter of crystal grain of the steel plate after hot rolling, and raises subsequent cold rolling and the deep drawability after annealing, it adds as occasion demands. When adding, it is made to contain more than 0.003 % desirably. If it adds superfluously, the grain growth at the time of annealing will be checked, and workability will be worsened. For this reason, that upper limit is made into 0.02%.

[0030] aluminum : it is used in order [for deoxidation of steel] to fix and defang N which is an unescapable impurity. If the content is ineffective at under 0.005 % and exceeds 0.1 %, effectiveness is not only saturated, but an oxide will be formed on the surface of a base material at the time of reduction annealing, and it is Zn at the time of hot dipping. Wettability is spoiled. For this reason, aluminum The range of a content is made into 0.005% - 0.1%.

[0031] B: It is not necessary to add. However, since there is effectiveness which inhibits the brittle fracture after press working of sheet metal which is easy to produce when processing IF steel of super-low C in B, it is made to contain as occasion demands. In order to acquire the effectiveness, it is desirable to make it contain 0.0005% or more. Since the effectiveness is not only saturated, but it controls generation of a crater and the workability of a steel plate is checked even if it makes it contain superfluously, the upper limit is made into 0.005%.

[0032] In addition, little direction of the element mixed as an unescapable impurity, for example, S, N, etc., is good, and it is desirable for S to consider and for N to consider as 0.004% or less 0.015% or less.

[0033] (2) Plating coat aluminum Content: There is effectiveness which enlarges the increase of the crater of a plating coat front face and the number of trough peaks. In order to obtain the necessary

number of trough peaks, it is aluminum in a plating coat. A content is made into 0.18% or more. It is aluminum in a plating coat. If it is made to contain, it is Fe-Zn to an interface with a base material. An alloy layer is formed and the alloying reactivity in crystal grain is reduced. This becomes easy to produce a crater. aluminum in a plating coat If a content becomes superfluous, the number of trough peaks will increase remarkably and the image clarity after paint will be spoiled. Moreover, when using IF steel of super-low C as a base material, it is aluminum in a plating coat. If a content becomes superfluous, alloying will be delayed too much and alloying will take long duration to it. For this reason, that upper limit is made into 0.50%.

[0034] Fe Content: Fe in a plating coat Although a content is not specified by this invention, in order to keep good powdering-proof nature and chipping-proof nature, it is desirable to manage in 7 - 18% of range.

[0035] Arithmetic-mean granularity of a plating coat front face (Ra): Use a three-dimension granularity measuring instrument and it is 0.8mm. Filtering excepts the above external waviness component, and it measures and asks for the plating front face of 10mm around with the ten or more scanning lines. Ra 1 micrometer If it exceeds, the image clarity after paint falls and it is unsuitable as a steel plate for sheathing of an automobile. For this reason, Ra of the steel plate of this invention 1 micrometer It considers as the following.

[0036] The number of trough peaks of a plating coat front face: A three-dimension granularity measuring instrument is used for the number of trough peaks like the above, and it is 0.8mm. Counting is carried out using the datum line formed in 50% of location of the maximum depth from the cross-section curve, its granularity average line, and granularity average line of the front face which excepted the above external waviness component by filtering, and obtained it. After a cross-section curve goes up to a forward side rather than a granularity average line, it carries out counting, using the time of exceeding the datum line of a negative side to a negative side further as one trough, and let the sum total of the number of troughs per 25.4mm of measurement length be the number of trough peaks. The sliding frictional resistance falls and a flaking stops being able to produce it easily as the number of trough peaks of a plating steel plate becomes large. The minimum of the number of trough peaks is set to 320 / 25.4mm as a limitation which a flaking does not produce. On the other hand, if the number of trough peaks becomes large too much, the image clarity after paint will be spoiled. For this reason, that upper limit is set to 600 / 25.4mm.

[0037] (3) As a base material of the steel plate of manufacture approach this invention, the cold rolling plate of the steel of the chemical composition indicated above (1) is suitable. However, it is good also considering the steel plate which annealed this cold rolling plate, or the hot rolled steel plate from which the oxide film was removed as a base material. Generally the facility for giving hot dip zincing is easy to be used. After degreasing a base material with alkaline degreasing etc., hot dipping of the reduction annealing is performed and carried out. Alloying processing is performed after that and it considers as a product. The suitable manufacture condition is shown below.

[0038] A facility of general alkali cleaning etc. may be enough for pretreatment of the base material in front of hot dip zincing. The temperature up of the base material which pretreated is carried out in a reducing atmosphere more than 600 **. When you need recrystallization annealing, it performs reduction annealing which it heats [annealing] more than recrystallizing temperature and makes recrystallization complete. After that, in process of cooling, hot dipping is performed, after holding in a reducing atmosphere for 20 - 60 seconds to the temperature requirement of 600 - 500 ** (maintenance by this 600 - 500 ** is hereafter described as "low-temperature maintenance"). Thereby, the increase of a crater and the effectiveness of improving the image clarity after paint become remarkable.

[0039] Especially the ambient atmosphere at the time of this low-temperature maintenance has desirable dew-point-20--40 degree C in the ambient atmosphere of six to hydrogen concentration 12 volume %, and ******. Moreover, it is suitable to make a base material pile up for 20 - 60 seconds in the above-mentioned ambient atmosphere in the temperature requirement of 600 - 500 **. The case where the hydrogen concentration of an ambient atmosphere exceeds 12 volume %, and a dew-point - When low, or when neither the case where retention temperature does not fulfill 500 **, nor the holding time fulfills

20 seconds more than 40 degrees C, generation of a crater will be inadequate, the numbers of trough peaks will run short, flaking-proof nature will not be improved, and the image clarity after paint will not improve, either. On the other hand, the hydrogen concentration of an ambient atmosphere does not fulfill 6 volume %, or a dew-point - When becoming high exceeding 20 degrees C, or when retention temperature exceeds 600 ** or the holding time exceeds 60 seconds, the amount of surface oxides becomes the cause which the roll for base material conveyance in increase and a furnace is polluted with an oxide, and surface cracks, such as an abrasion, generate. If the holding time exceeds 60 seconds, operation nature will worsen and will also spoil economical efficiency.

[0040] Subsequently, after cooling even to the temperature near the plating bath, hot dipping is immersed and carried out to a plating bath, and alloying processing is performed. It is aluminum in a plating coat. In order to do 0.18-0.5 % content of, it is desirable to galvanize aluminum using the plating bath contained 0.11 to 0.14%. In addition, aluminum under plating bath here A content is aluminum in dross. It does not contain.

[0041] Plating coating weight has common 20 - 70 g/m2, and its this invention is also good at comparable plating coating weight. 480 - 600 ** is desirable, and the temperature of the plating steel plate at the time of alloying is Fe-Zn further. It is desirable especially to carry out above 520 ** to which zeta phase (FeZn13) which is one sort of an alloy phase disappears. This is because the direction with few zeta phases is good for the surface section of a plating coat, in order to make a flaking hard to produce. Fe of a plating coat As for a content, it is desirable to make it 7 - 18% of range by the average of the whole plating coat.

[0042] In order to correct or adjust the mechanical property of a steel plate, flatness, and a configuration, it is desirable to perform slight rolling (skin pass rolling) after alloying processing. The effectiveness that image clarity improves by this is also expectable. Skin pass rolling may also be lubrication rolling (dry rolling) or non-lubrication rolling (wet rolling). Moreover, leveler plate-leaping processing usually performed may be performed.

[0043]

[Example]

(Example 1) The steel of the chemical composition shown in Table 1 was ingoted, hot rolling and cold rolling were performed, and the coiled form steel plate of thickness 0.8 mm and width-of-face 200 mm was obtained.

[0044]

[Table 1]

表1

鋼	母材の化学組成（重量%）（残部：不可避不純物およびFe）								備考
	C	Si	Mn	P	Ti	Nb	Al	B	
A	0.0031	0.030	0.15	0.008	0.025	-	0.030	-	
B	0.0023	0.047	0.10	0.008	0.035	0.007	0.021	-	本
C	0.0023	0.040	0.10	0.008	0.030	0.007	0.020	0.0008	発
D	0.0035	0.070	0.15	0.010	0.018	0.008	0.025	-	明
E	0.0018	0.085	0.25	0.012	0.022	0.008	0.033	-	例
F	0.0025	0.110	0.15	0.015	0.044	0.010	0.050	-	
G	0.0021	0.112	0.35	0.012	0.040	0.010	0.050	0.0011	
H	0.0022	0.130	0.38	0.019	0.046	0.015	0.020	-	
I	0.0020	0.128	0.11	0.020	0.036	0.018	0.020	-	
*J	0.0022	*0.001	0.30	0.010	0.018	-	0.030	-	
*K	0.0025	*0.001	*0.42	0.012	0.020	-	0.035	-	比
*L	0.0018	0.031	*0.52	0.012	0.035	0.005	0.035	-	較
*M	0.0032	0.032	0.21	*0.028	0.041	-	0.035	-	例
*N	0.0040	0.032	0.21	0.015	0.010	-	0.035	-	

(注) *印は本発明の条件を外れるものであることを示す。

[0045] It degreased in the sodium-hydroxide water solution 10% through this to washing Rhine. Furthermore, the hot-dipping facility for an experiment with a direct fire reducing furnace is used, and

h g cg b eb cg e e

they are hydrogen 10 volume %, nitrogen 90 volume %, and a dew-point. - After having given reduction annealing held for 60 seconds to 850 ** in the 30-degree C ambient atmosphere, cooling in the range of 600-500 degrees C and making it pile up for 10 - 60 seconds in this range, it cooled to 440 - 520 **, and hot dipping was performed. Plating coating weight sprayed high pressure gas, and adjusted it to 40**5g per one side/m2. aluminum of a plating bath The content made temperature of a plating bath 460 ** 0.12 to 0.15%. Furthermore, it heats to the steel plate attainment temperature 480 - 580 ** by induction heating, it holds for 20 seconds in this temperature requirement, and is Fe of a plating coat. The content was adjusted to 8 - 15% of range.

[0046] Measurement of the chemical composition of a plating coat: The chemical composition in a coat is 0.1. The plating coat was dissolved in 10% of the weight of the hydrochloric-acid water solution containing the inhibitor of weight %, and it asked by performing solution analysis.

[0047] Measurement of surface roughness: Arithmetic mean granularity (Ra) was measured with the three-dimension granularity meter [the surfboard COM by Tokyo Seimitsu [Co., Ltd.] Co., Ltd.]. 1 micrometer With the contact needle, they could be the scan speed of 0.06mm/second, ten scan numbers, and measurement area 10mmx10mm.

[0048] The number of trough peaks asked for the number of troughs using the same measuring instrument from the cross-section curve which removed the external waviness component more than 0.8 mm with a measurement die length of 25.4mm.

[0049] Measurement of coefficient of friction: Coefficient of friction (mu) was measured using the sliding nature evaluation equipment shown in drawing 1 . The test piece 1 of width of face of 30mm and die-length 270 mm is held between the dice 2 of sliding nature evaluation equipment, and the blank holder bead 4 of a hemicycle with a radius of 5mm, punch 3 is pressed fit, applying a blank holder load (P), and a test piece 1 is fabricated to the character type of KO. A blank holder load is 750, 1000, 1250, and 1500kgf. It considered as four conditions. The maximum (F) of the insertion pressure of the punch 3 in each case was calculated, and it asked for coefficient of friction by following ** type from the increment (dP) of a blank holder load, and the increment (dF) of the maximum of punch insertion pressure.

[0050] A dice 2, the blank holder bead 4, and the front face of punch 3 are #600. What was ground with abrasive paper was used. Slushing oil was applied to both sides of a test piece 1 two times 2.5 g/m per one side as lubricant, and the press fit rate of punch 3 was considered as a part for 60mm/.

[0051] mu=dF / 2dP---- less than [**mu:0.24]: -- O less than [0.24 super-0.28]: -- less than [O0.28 super-0.32]: -- ** 0.32**: -- flaking-proof [x] nature investigation: -- it evaluated using the sliding nature evaluation equipment shown in drawing 1 . The test piece 1 of width of face of 30mm and die-length 270 mm is held between a dice 2 and the blank holder bead 4, and they are 1000kgf(s) about a blank holder load. It carries out, punch 3 is pressed fit and a test piece 1 is fabricated to the character type of KO. Slushing oil was applied to both sides of a test piece 1 two times 2 g/m per one side as lubricant, and the press fit rate of punch 3 was considered as a part for 60mm/. Adhesive tape was stuck on the front face of the side pressed down by the bead of the side-attachment-wall section of the test piece fabricated by the character type of KO, the situation of the piece of exfoliation of the plating coat adhering to a tape was judged visually, and the following partition estimated.

[0052] Those without a flaking: O 20 micrometers of under coats according to a cation mold electrodeposition paint to the steel plate which exists slightly and performed image clarity trial:immersion type phosphating after :x paint with :** flaking 35-40 micrometers of middle coats 35-40 micrometers of finishing Three quart paint (sum-total thickness: 100 mum extent) was performed. It measured using the map visibility measuring device [the NSIC mold by Suga Test Instruments Co., Ltd.] by having made the map visibility of this test piece into the NSIC value, and the following partition estimated. in addition, a NSIC value -- blackboard polish glass -- 100 it is -- a NSIC value -- 100 Such good image clarity is shown that it is near.

[0053]

ＮＳＩＣ値　95以上：◎　　94～85：○
　　80～85：△　　80未満：×

Various kinds of performance-evaluation results are shown in Table 2.
[0054]
[Table 2]
表2

試番	鋼種	めっき条件			めっき皮膜構成				性能評価結果					備考
		雰囲気露点(℃)	低温保持(秒)	めっき浴Al(重量%)	化学組成 Al(重量%)	化学組成 Fe	表面粗さ Ra(μm)	表面粗さ 谷ピーク数	摺動性 摩擦係数(μ)	摺動性 評価	耐フレーキング性	鮮映性 NSIC値	鮮映性 評価	
1	A	−20	40	0.12	0.18	8	0.78	403	0.245	○	○	93	○	
2	A	−30	50	0.13	0.30	10	0.82	521	0.222	◎	○	85	○	本
3	B	−35	50	0.13	0.25	9	0.80	482	0.203	◎	○	88	○	発
4	B	−40	55	0.14	0.38	12	0.92	550	0.191	◎	○	86	○	明
5	B	−30	60	0.12	0.38	12	0.94	550	0.191	◎	○	88	○	例
6	C	−40	40	0.12	0.22	12	0.80	450	0.238	◎	○	96	◎	
7	C	−25	50	0.13	0.35	10	0.85	480	0.212	◎	○	95	◎	
8	C	−20	60	0.14	0.48	10	0.94	585	0.206	◎	○	85	○	
9	D	−30	40	0.12	0.20	12	0.78	420	0.255	○	○	97	◎	
10	D	−40	50	0.13	0.32	9	0.88	498	0.230	◎	○	95	◎	
11	E	−35	40	0.12	0.18	10	0.75	380	0.268	○	○	96	◎	
12	E	−40	50	0.12	0.25	12	0.80	455	0.233	◎	○	98	◎	
13	E	−40	60	0.14	0.50	12	0.93	596	0.210	◎	○	95	◎	
14	F	−40	20	0.12	0.22	9	0.73	320	0.278	○	○	96	◎	
15	F	−40	50	0.13	0.41	10	0.90	510	0.228	◎	○	88	○	
16	G	−35	50	0.13	0.35	13	0.93	538	0.210	◎	○	92	○	
17	H	−30	60	0.14	0.47	9	0.94	585	0.201	◎	○	85	○	
18	I	−20	20	0.12	0.20	11	0.78	350	0.271	○	○	98	◎	
19	I	−25	40	0.13	0.30	15	0.85	452	0.230	◎	○	95	◎	
20	I	−23	60	0.13	0.45	10	0.93	569	0.212	◎	○	95	◎	
21	*J	−40	40	0.13	0.35	10	*1.15	380	0.280	△	△	78	×	
22	*J	−40	*10	0.12	*0.15	10	0.72	*265	0.325	×	×	90	○	比
23	*K	−40	50	0.13	0.40	11	*1.20	398	0.265	○	○	75	×	較
24	*L	−30	50	0.13	0.38	12	*1.08	350	0.285	△	△	80	△	例
25	*M	−40	60	0.13	0.28	9	*1.05	*280	0.320	×	×	83	△	
26	*N	−35	40	0.12	0.20	12	0.90	*310	0.295	△	△	86	○	
27	A	−40	*15	0.14	*0.52	12	*1.12	*680	0.195	◎	○	75	×	
28	B	−40	50	0.12	*0.16	8	0.90	*310	0.296	△	△	98	◎	
29	B	−40	*15	0.12	0.20	10	0.98	*310	0.280	△	△	80	△	

（注）＊印は本発明の条件を外れるものであることを示す。

[0055] Both the image clarity after also painting flaking-proof nature of the test numbers 1-20 which fulfill the conditions as which this invention specifies the chemical composition and the plating coat configuration of a base material as shown in Table 2 is also good.
[0056] Si Mn The test numbers 21 and 23 using the steel J and K with which the content has separated from the conditions which this invention specifies are inferior in the image clarity after paint. Si A content is low and it is aluminum in a plating coat. The number of trough peaks does not fill the value which this invention specifies with the test number 22 which has separated from the range where this invention also specifies a content, and its flaking-proof nature is not desirable. Mn The test number 24 contained superfluously and the test number 25 of a gap which P contains superfluously are not [flaking-proof nature] desirable. Ti The dissolution C in steel segregates the test number 26 using the steel N for which the content was insufficient to a grain boundary, it runs short of the numbers of trough peaks, and its flaking-proof nature is not desirable.

h　　g　cg b　　eb cg e e

[0057] For the chemical composition of a base material, a test number 27 is aluminum in a plating coat, although it is condition within the limits which this invention specifies. The image clarity after painting, since the content is over the upper limit of the range which this invention specifies is inferior. Also for a test number 28, the chemical composition of a base material is aluminum in a plating coat, although this invention is condition within the limits as which it specifies. Since there are too few contents, flaking-proof nature is inferior. Since the time amount at the time of low-temperature maintenance was insufficient for the test number 29, its flaking-proof nature is not desirable.

[0058]

[Effect of the Invention] It is hard to generate the poor flaking at the time of press working of sheet metal, and the steel plate of this invention is excellent in the image clarity at the time of painting. If this is used as a material of the exterior parts of an automobile, the yield and workability in a processing process are excellent, and the exterior check as products of an automobile is also excellent. Moreover, according to the approach which this invention specifies, this steel plate can be manufactured economically and rationally.

[Translation done.]

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(54)【発明の名称】　合金化溶融亜鉛めっき鋼板およびその製造方法

(57)【要約】
【課題】主として自動車に使用される、塗装鮮映性とめっき皮膜の耐フレーキング性が優れた合金化溶融亜鉛めっき鋼板を提供する。
【課題手段】Ｃ：0.004 %以下、Ｓｉ：0.03～0.13%、Ｍｎ：0.05～0.4 %、Ｐ：0.007 ～0.02%、Ｔｉ：0.018 ～0.05%、Ｎｂ：0～0.02%、Ａｌ：0.005 ～0.1 %、Ｂ：0～0.005 %の鋼を母材とし、Ａｌを0.18%以上0.5 %以下含有し、表面粗さが算術平均粗さ(Ｒａ)で１μｍ以下、谷ピーク数：320 ～600 ／25.4mmであるＦｅ－Ｚｎ合金めっき皮膜を有する合金化溶融亜鉛めっき鋼板、および、－20～－40℃の露点の水素と窒素からなる還元性雰囲気中で600 ～500 ℃の温度範囲に20秒以上母材を滞留させる工程を含み、0.11重量%以上0.14重量%以下のＡｌを含有するめっき浴を用いる製造方法。

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【特許請求の範囲】

【請求項1】重量%でC：0.004 %以下、Si ：0.03～0.13%、Mn ：0.05～0.4 %、P：0.007 ～0.02%、Ti ：0.018 ～0.05%、Nb ：0～0.02%、Al ：0.005～0.1%、B：0～0.005%、残部はFe および不可避不純物からなる鋼を母材とし、少なくともその片面に、Al を0.18%以上0.5 %以下含有し、その表面粗さが算術平均粗さ(Ra)で1μm 以下、谷ピーク数：320 ～600 /25.4mmであるFe －Zn 合金めっき皮膜を有することを特徴とする塗装鮮映性および耐フレーキング性に優れた合金化溶融亜鉛めっき鋼板。

【請求項2】母材をめっき前に加熱する工程において、露点が－20～－40℃の範囲である水素と窒素からなる還元性雰囲気中で600 ～500 ℃の温度範囲に20秒以上60秒以下母材を滞留させる工程を含み、かつ、0.11重量%以上0.14重量%以下のAl を含有するめっき浴を用いて亜鉛めっきした後に合金化処理を施すことを特徴とする請求項1に記載の合金化溶融亜鉛めっき鋼板の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、加工時の耐めっき剥離性と塗装後の鮮映性とに優れる、主として自動車用に使用される合金化溶融亜鉛めっき鋼板およびその製造方法に関する。

【0002】

【従来の技術】近年、家電、建材、及び自動車の産業分野においては溶融亜鉛めっき鋼板が大量に使用されている。とりわけ経済性、防錆機能、塗装後の性能の点で合金化溶融亜鉛めっき鋼板が広く用いられている。

【0003】通常、溶融亜鉛めっき鋼板は、母材に適当な脱脂洗浄を施し、水素および窒素からなる還元性雰囲気で焼鈍し、めっき温度付近まで冷却して溶融亜鉛浴に浸漬することにより製造される。合金化溶融亜鉛めっき鋼板は、溶融亜鉛めっきした鋼板を500 ～600 ℃で3～60秒間加熱して母材のFe を亜鉛めっき層に拡散させ、Fe －Zn 合金層を形成させて製造する。一般に、めっき層の平均のFe 含有量は8～12重量%であり、めっき付着量は片面当り20～70g／m²である。付着量がこの範囲を下回るものは通常の手段において製造することが難しく、また、この範囲を上回るものはめっき層の耐パウダリング性を確保することが困難であるので一般には供給されていない。

【0004】このようにして製造された合金化溶融亜鉛めっき鋼板は、プレス加工を行ない所定の形状に加工されて塗装される。プレス加工時に生じやすいパウダリング、フレーキングおよび塗装後の使用時に生じやすい低温チッピングを防ぐために、この合金化溶融亜鉛めっき鋼板にはめっき皮膜の密着性が要求される。

【0005】また、塗装された製品の仕上がり外観が良いことも重要視され、その指標である塗装後の鮮映性が

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良い鋼板も求められている。

【0006】パウダリングはプレス加工時に鋼板が圧縮変形を受ける領域でめっき皮膜が粉状になって剥離する現象である。パウダリングが生じるとその部分の耐食性が劣化し、発生したZn 粉末が金型に付着して成形品の外観品質を損なう。合金化の過程でFe －Zn 合金が発達しすぎてΓ相等の硬質のFe －Zn 合金層が過剰に生じるとパウダリングが顕著になるといわれている。パウダリングはめっき付着量、合金化度等を管理して改善が図られてきた。

【0007】低温チッピングは、0℃以下の低温域で自動車の車体に高速で小石が衝突した時等に、母材との界面からめっき皮膜が塗膜と共に剥離する現象である。これはめっき皮膜と母材表面との密着性の問題であり、低温チッピング性を改善するために、めっき皮膜と接する母材表面の粗さを調整する方法等が提案されている。

【0008】プレス加工の際には鋼板が金型の表面を摺動する。この時にめっき皮膜の一部が薄片状になって剥離することがある。この現象をフレーキングと称している。フレーキングが生じると成形品の外観品質や耐食性を損なうだけでなく、プレス加工時のしわ押さえ圧力が変動し、プレス破断や形状不良等の原因にもなる。フレーキングが発生する原因は、めっき皮膜の脆弱性やめっき皮膜と母材表面との間の密着不良等にもあるが、最も大きく影響するのは、鋼板と、鋼板の流入を阻害する金型との間の摩擦抵抗である。

【0009】フレーキングを防止する方法として、めっき皮膜の表面粗さを粗くして、プレス加工時の潤滑剤の保持性を向上させることが考えられるが、この方法はめっき皮膜の表面粗さが粗くなり、自動車の外装用途として重要な品質である塗装後の鮮映性が損なわれるのが問題である。

【0010】フレーキングに対する改善策として、例えば特開平05－236984号公報に記載されているように、合金化溶融亜鉛めっき皮膜の上にFe の薄膜を電気めっきしてめっき鋼板のすべり性を改善する方法がある。しかしこの方法では、溶融めっき鋼板の上にさらに電気めっきを施さなければいけないので経済性が損なわれる。

【0011】

【発明が解決しようとする課題】本発明が解決しようとする課題は、主として自動車に使用される合金化溶融亜鉛めっき鋼板に関するもので、塗装後の鮮映性とめっき皮膜の耐フレーキング性とに優れた合金化溶融亜鉛めっき鋼板およびその製造方法を提供することである。

【0012】

【課題を解決するための手段】本発明の要旨は下記の（1）に記載した塗装鮮映性および耐フレーキング性に優れた合金化溶融亜鉛めっき鋼板、および（2）に記載したその製造方法にある。

【0013】（1）重量%でC：0.004 %以下、Si ：

0.03～0.13%、Mn ：0.05～0.4 %、P：0.007 ～0.02 %、Ti ：0.018 ～0.05%、Nb ：0～0.02%、Al ：0.005 ～0.1%、B：0～0.005%、残部はFe および不可避不純物からなる鋼を母材とし、少なくともその片面に、Al を0.18%以上0.5 %以下含有し、その表面粗さが算術平均粗さ（Ra ）で1μm 以下、谷ピーク数：320～600 ／25.4mmであるFe －Zn 合金めっき皮膜を有することを特徴とする塗装鮮映性および耐フレーキング性に優れた合金化溶融亜鉛めっき鋼板。

【００１４】（２）母材をめっき前に加熱する工程において、露点が－20～－40℃の範囲である水素と窒素からなる還元性雰囲気中で600 ～500 ℃の温度範囲に20秒以上60秒以下母材を滞留させる工程を含み、かつ、0.11重量%以上0.14重量%以下のAl を含有するめっき浴を用いて亜鉛めっきした後に合金化処理を施すことを特徴とする上記（１）に記載の合金化溶融亜鉛めっき鋼板の製造方法。

【００１５】本発明者等は、めっき皮膜の諸特性に関する以下の知見を得て本発明を完成させた。

【００１６】① めっき皮膜の表面には、台地状あるいは断続的な土手状の凸部と、直径が2～20μm 前後の微小な凹み部とがある。この凸部は母材表面の結晶粒界を中心にして生じているものが多く、凹み部は逆に母材表面の結晶粒内に相当する位置に多く認められる。この凸部は合金化後に施されるスキンパス圧延やレベラー通板等の影響などを受けて、その頂部が平面状になっているものが多い。他方凹み部には合金めっきの結晶粒が観察され、合金化反応後の表面を維持しているように思われる。以下、このめっき表面の微小な凹み部を「クレーター」と記す。

【００１７】めっき皮膜表面の凸部あるいはクレーターは、母材とめっき皮膜との間のFe－Zn 合金化反応性が母材の結晶粒内と粒界とで異なることによって生じる。結晶粒界の方が結晶粒内に較べて反応性が高いので、粒界ではFe －Zn 合金化反応が早く進行し、粒界上部に相当する部分のめっき皮膜が凸状になる。クレーターは相対的に合金化反応が遅い結晶粒内相当部に多くなる。

【００１８】② めっき皮膜表面のクレーターの発生頻度は、表面粗さの断面曲線測定で求められる谷ピーク数（ここでは測定長25.4mmの間に測定される、その谷の深さが最も深い谷の深さの50%を超える谷数）と対応がある。クレーターの数が増すにつれて谷ピーク数が大きくなり、谷ピーク数が大きいものほど摩擦係数が小さく、フレーキングが発生しにくい。

【００１９】③ 極低C鋼にTi やNb を添加して鋼中のCを析出物として固定し、さらにPやB含有量を制限した鋼を母材にし、Al 含有量の高い亜鉛めっき浴を用いて溶融めっきした後合金化することで、クレーターの数を増し、谷ピーク数を大きくすることができる。これは、めっき皮膜のAl 含有量が高い場合には、母材表面での結晶粒界と結晶粒内との間の合金化反応速度の差が拡大されるためであると推測される。

【００２０】④ このようにめっき皮膜の表面にクレーターが多いと、一般的には、表面粗さが粗くなり、塗装後の鮮映性が劣化し、外装用途には好ましくなくなる。しかし、母材に適量のSi を含有させ、めっき前の加熱工程において、再結晶が終了した母材を特定の還元性雰囲気中で低温保持し、その後にめっきし合金化処理すれば、めっき表面のクレーターを増したうえに塗装後の鮮映性を改善させることができる。

【００２１】この理由は、以下のように推定される。Fe －Zn 合金化反応性は、母材の結晶集合組織の影響を受ける。このため、母材表面には、その集合組織の差によって、合金化の反応性が高い結晶と低い結晶が存在している。反応性が高い結晶、例えば、結晶体の｛１００｝面が母材表面と平行に集積している｛１００｝集合組織の結晶では、粒界と粒内との間の反応性の差が少ないためにクレーターが生じにくい。他方、反応性が低い結晶、例えば、結晶体の｛１１１｝面が母材表面と平行に集積している｛１１１｝集合組織の結晶では、粒界と粒内との間の反応性の差が大きいために、より明瞭にクレーターが生じる。

【００２２】Si を添加した鋼では、還元焼鈍時に母材最表層部にSi 酸化物が濃化し、結晶表面での合金化反応性が低下する。この時、反応性が高い集合組織の結晶ほど反応性が大きく低下する。Si 酸化物の濃化により粒界の反応性も低下する傾向にあるが、結晶粒内の反応性の方がより大きく低下する。このため、粒界と粒内との反応性の差が拡大し、Si を添加しない鋼よりも多数のクレーターが認められるようになる。さらに、反応性が高い集合組織の結晶の反応性が特に大きく低下するために結晶間での反応性の差が小さくなり、クレーターの深さの差が縮小してめっき表面の算術平均粗さが減少するものと考えられる。

【００２３】

【発明の実施の形態】本発明の実施に際し、各要因や条件を限定した理由を以下に述べる。なお、以下に記す%表示は重量%を意味する。

【００２４】（１）鋼板の化学組成

C：鋼板の加工性を損うので、C含有量は少ないほど好ましい。また、鋼中に固溶しているCは、母材の結晶粒界に偏析して結晶粒界でのFe －Zn 合金反応を遅らせ、結果的にクレーターの生成を抑制する作用がある。本発明では鋼板の加工性とめっき皮膜表面の谷ピーク数とを確保するために、Ti やNb を含有させてCを固定し無害化する。C含有量が増すと、Ti やNb を多量に添加しなければならないので経済性に欠けるうえ、炭化物が過剰に増加して鋼板の加工性も損う。このため、C含有量の上限は0.004 %とする。好ましくは0.003 %以

下である。

【００２５】Si ：適量のSi を含有させると母材を還元焼鈍する時に母材表面にSi 酸化物を生じさせることでめっき皮膜表面のクレーターを増加させる。これにより加工時に使用する潤滑剤の保持性が向上しフレーキングが防止できる。同時に、皮膜表面の表面粗さを減少させて塗装後の鮮映性を改善する効果もある。これらの効果を得るためにその下限を0.03%とする。母材表面のSi 酸化物が過剰になると結晶粒内と粒界との間の合金化反応性の差が減少し、谷ピーク数が過度に減少する。このため、その上限を0.13%とする。

【００２６】Mn ：不可避不純物として鋼中に混入してくるSに起因する熱間脆性を抑止するため、0.05%以上含有させる。過剰に添加すると、鋼板の加工性が損なわれるので、その上限を0.4 %とする。

【００２７】P：加工性を損なわないで鋼板の強度を高めるのに好適な元素である。本発明ではクレーターを増し谷ピーク数を確保するために極低CのＩＦ鋼（Interstitial Free 鋼）を用いる。しかし、自動車車体用の鋼板としてはある程度の強度が必要であるので、Pを含有させて強度を保持する。そのため、P含有量の下限を0.007 %とする。Pを過剰に添加すると母材の結晶粒界に偏析し、粒界での合金化反応を抑制して谷ピーク数が減少する。このため、P含有量の上限を0.02%とする。

【００２８】Ti ：極低C鋼の固溶Cを固定し、結晶粒界での合金化反応性を高めるために0.018 %以上含有させる。過剰に添加すると経済性を損なうのでその上限を0.05%とする。

【００２９】Nb ：無添加でもよいが、Ti と同様に固溶Cを固定する効果や、熱間圧延後の鋼板の結晶粒径を小さくして、その後の冷間圧延および焼鈍後の深絞り性を高める効果があるので必要により添加する。添加する場合には、望ましくは、0.003 %以上含有させる。過剰に添加すると、焼鈍時の結晶粒成長を阻害し加工性を悪くする。このため、その上限は0.02%とする。

【００３０】Al ：鋼の脱酸のため、および不可避不純物であるNを固定して無害化するために用いられる。その含有量が0.005 %未満では効果がなく、0.1 %を超えると効果が飽和するばかりでなく、還元焼鈍時に母材の表面に酸化物を形成し、溶融めっき時にZn の濡れ性が損なわれる。このため、Al 含有量の範囲を0.005%～0.1%とする。

【００３１】B：添加しなくても良い。しかし、Bには、極低CのＩＦ鋼を加工する場合に生じやすいプレス加工後の脆性破壊を抑止する効果があるので、必要により含有させる。その効果を得るためには0.0005%以上含有させることが望ましい。過剰に含有させてもその効果が飽和するばかりでなく、クレーターの生成を抑制し、鋼板の加工性をも阻害するので、その上限を0.005%とする。

【００３２】その他、不可避不純物として混入する元素、例えば、SやN等は少ない方がよく、Sは0.015%以下、Nは0.004%以下とすることが望ましい。

【００３３】（２）めっき皮膜

Al 含有量：めっき皮膜表面のクレーターを増し、谷ピーク数を大きくする効果がある。所要の谷ピーク数を得るために、めっき皮膜中のAl 含有量は0.18%以上とする。めっき皮膜中にAl を含有させると母材との界面にFe －Zn 合金層が形成され、結晶粒内の合金化反応性を低下させる。これによりクレーターが生じやすくなる。めっき皮膜中のAl 含有量が過剰になると谷ピーク数が著しく増加し塗装後の鮮映性が損なわれる。また、母材として極低CのＩＦ鋼を用いる場合には、めっき皮膜中のAl 含有量が過剰になると合金化が過度に遅延し、合金化に長時間を要する。このため、その上限を0.50%とする。

【００３４】Fe 含有量：めっき皮膜中のFe 含有量は本発明で特定するものではないが、耐パウダリング性や耐チッピング性を良好に保つために、７～１８%の範囲に管理するのが好ましい。

【００３５】めっき皮膜表面の算術平均粗さ（Ra）：３次元粗さ測定器を用い、0.8㎜ 以上のうねり成分をフィルター処理により除外して10㎜四方のめっき表面を走査線10本以上で測定して求める。Ra が１μm を超えると塗装後の鮮映性が低下し、自動車の外装用鋼板としては不適当である。このため本発明の鋼板のRa は１μm 以下とする。

【００３６】めっき皮膜表面の谷ピーク数：谷ピーク数は、上記と同様に３次元粗さ測定器を用い、0.8㎜ 以上のうねり成分をフィルター処理により除外して得た表面の断面曲線とその粗さ平均線、および、粗さ平均線から最大深さの50%の位置に設けた基準線とを用いて計数する。断面曲線が粗さ平均線よりも正側に上がった後、負側の基準線をさらに負側に超えた時を１谷として計数し、測定長25.4㎜当たりの谷数の合計を谷ピーク数とする。めっき鋼板の谷ピーク数が大きくなるにつれてその摺動摩擦抵抗は低下し、フレーキングが生じ難くなる。フレーキングが生じない限界として谷ピーク数の下限を320 ／25.4㎜とする。他方、谷ピーク数が大きくなりすぎると塗装後の鮮映性が損なわれる。このため、その上限を600 ／25.4㎜とする。

【００３７】（３）製造方法

本発明の鋼板の母材としては、上記（１）に記載する化学組成の鋼の冷間圧延板が好適である。しかし、この冷間圧延板を焼鈍した鋼板、または、酸化皮膜を除去した熱間圧延鋼板等を母材としてもよい。溶融亜鉛めっきを施すための設備は一般に使用されるものでよい。母材をアルカリ脱脂等で脱脂した後、還元焼鈍を行ない溶融めっきする。その後合金化処理を行なって製品とする。その好適な製造条件を以下に示す。

【００３８】溶融亜鉛めっき前の母材の前処理は一般的なアルカリ洗浄等の設備で十分である。前処理を施した母材を還元性雰囲気の中で600 ℃以上に昇温する。再結晶焼鈍を必要とする場合には再結晶温度以上に加熱して再結晶を完了させる還元焼鈍を行なう。その後冷却の過程で、600 ～500 ℃の温度範囲に20～60秒間、還元性雰囲気の中で保持した後に溶融めっきを施す（以下、この600 ～500 ℃での保持を「低温保持」と記す）。これにより、クレーターを増し、かつ、塗装後の鮮映性を改善する効果が顕著になる。

【００３９】この低温保持時の雰囲気は、水素濃度６～12体積%、残窒素の雰囲気で露点―20～―40℃が特に好ましい。また、上記の雰囲気で、600 ～500 ℃の温度範囲で20～60秒間母材を滞留させるのが好適である。雰囲気の水素濃度が12体積%を超える場合や露点が―40℃を超えて低い場合、あるいは保持温度が500 ℃に満たない場合や保持時間が20秒に満たない場合には、クレーターの生成が不十分で谷ピーク数が不足し耐フレーキング性が改善されず、塗装後の鮮映性も向上しなくなる。他方、雰囲気の水素濃度が６体積%に満たなかったり、露点が―20℃を超えて高くなる場合、あるいは、保持温度が600 ℃を超えたり保持時間が60秒を超える場合には、表面の酸化物量が増し、炉内の母材搬送用ロールが酸化物で汚染されて擦り傷等の表面疵が発生する原因になる。保持時間が60秒を超えると、操業性が悪くなって経済性も損なう。

【００４０】次いで、めっき浴近傍の温度にまで冷却後、めっき浴に浸漬して溶融めっきし合金化処理を施＊す。めっき皮膜中にAl を0.18～0.5 %含有させるために、Alを0.11～0.14%含有するめっき浴を用いてめっきすることが好ましい。なお、ここでのめっき浴中のAl 含有量は、ドロス中のAl を含まないものである。

【００４１】めっき付着量は20～70ｇ／m²が一般的であり、本発明も同程度のめっき付着量でよい。合金化時のめっき鋼板の温度は480 ～600 ℃が好ましく、さらに、Fe―Zn 合金相の１種であるζ相（FeZn13）が消失する520 ℃以上で行なうのが特に好ましい。これは、フレーキングを生じ難くするには、めっき皮膜の表層部にζ相が少ない方が良いからである。めっき皮膜のFe 含有量は、めっき皮膜全体の平均値で７～18%の範囲にするのが好ましい。

【００４２】鋼板の機械的性質や平坦、形状を修正あるいは調整するために、合金化処理後に軽度の圧延（スキンパス圧延）を施すことが望ましい。これにより鮮映性が向上する効果も期待できる。スキンパス圧延は潤滑圧延（ドライ圧延）でも、無潤滑圧延（ウエット圧延）でも構わない。また、通常行なわれているレベラー通板処理等を施しても構わない。

【００４３】

【実施例】

（実施例１）表１に示す化学組成の鋼を溶製し、熱間圧延と冷間圧延を施して厚さ0.8 mm、幅200 mmのコイル状の鋼板を得た。

【００４４】

【表１】

表1

鋼	母材の化学組成（重量%）（残部：不可避不純物およびFe）								備考
	C	Si	Mn	P	Ti	Nb	Al	B	
A	0.0031	0.030	0.15	0.008	0.025	-	0.030	-	
B	0.0023	0.047	0.10	0.008	0.035	0.007	0.021	-	本
C	0.0023	0.040	0.10	0.008	0.030	0.007	0.020	0.0008	発
D	0.0035	0.070	0.15	0.010	0.018	0.008	0.025	-	明
E	0.0018	0.085	0.25	0.012	0.022	0.008	0.033	-	例
F	0.0025	0.110	0.15	0.015	0.044	0.010	0.050	-	
G	0.0021	0.112	0.35	0.012	0.040	0.010	0.050	0.0011	
H	0.0022	0.130	0.38	0.019	0.046	0.015	0.020	–	
I	0.0020	0.128	0.11	0.020	0.036	0.018	0.020	–	
*J	0.0022	*0.001	0.80	0.010	0.018	-	0.030	–	
*K	0.0025	*0.001	*0.42	0.012	0.020	-	0.035	–	比
*L	0.0018	0.031	*0.52	0.012	0.035	0.005	0.035	–	較
*M	0.0032	0.032	0.21	*0.028	0.041	-	0.035	–	例
*N	0.0040	0.032	0.21	0.015	0.010	-	0.035	–	

（注）＊印は本発明の条件を外れるものであることを示す。

【００４５】これを洗浄ラインに通して10%水酸化ナトリウム水溶液で脱脂した。さらに、直火還元炉を持つ実験用溶融めっき設備を用いて、水素10体積%、窒素90体積%、露点―30℃の雰囲気中で850 ℃に60秒間保持する還元焼鈍を施し、600 ～500℃の範囲に冷却してこの範囲で10～60秒間滞留させた後、440 ～520 ℃まで冷却し※50※て溶融めっきを行なった。めっき付着量は、高圧ガスを吹き付けて片面当たり40±５ｇ／m²に調整した。めっき浴のAl 含有量は0.12～0.15%、めっき浴の温度は460 ℃とした。さらに、誘導加熱により鋼板到達温度480 ～580 ℃まで加熱し、この温度範囲で20秒間保持してめっき皮膜のFe 含有量を８～15%の範囲に調整した。

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【００４６】めっき皮膜の化学組成の測定：皮膜中の化学組成は0.1 重量%のインヒビターを含有する10重量%の塩酸水溶液中でめっき皮膜を溶解し、溶液分析を行って求めた。

【００４７】表面粗さの測定：３次元粗さ計［東京精密（株）社製サーフコム］により、算術平均粗さ（Ｒａ）を測定した。１μｍの接触針で、走査速度0.06㎜／秒、走査本数10本、測定面積10㎜×10㎜とした。

【００４８】谷ピーク数は同一の測定器を用い、測定長さ25.4㎜の、0.8 ㎜以上のうねり成分を除去した断面曲線から谷数を求めた。

【００４９】摩擦係数の測定：摩擦係数（μ）は図１に示す摺動性評価装置を用いて測定した。幅30㎜、長さ270 ㎜の試験片１を摺動性評価装置のダイス２と半径５㎜の半円形のしわ押さえビード４との間で保持し、しわ押さえ荷重（Ｐ）をかけてポンチ３を圧入し、試験片１をコの字型に成形する。しわ押さえ荷重は、750 、1000、1250、1500kgf の４条件とした。それぞれの場合のポンチ３の圧入力の最大値（Ｆ）を求め、しわ押さえ荷重の増分（ｄＰ）とポンチ圧入力の最大値の増分（ｄＦ）とから、下記①式によって摩擦係数を求めた。

【００５０】ダイス２、しわ押さえビード４およびポンチ３の表面は、＃600 の研磨紙で研磨したものを用いた。試験片１の両面には潤滑剤として防錆油を片面当たり2.5ｇ／㎡塗布し、ポンチ３の圧入速度は60㎜／分とした。

【００５１】$\mu = dF / 2dP$ ---- ①

μ：0.24以下：◎　　0.24超0.28以下：○
0.28超0.32以下：△　　0.32超：×

10

耐フレーキング性調査：図１に示す摺動性評価装置を用いて評価した。幅30㎜、長さ270 ㎜の試験片１をダイス２としわ押さえビード４との間で保持し、しわ押さえ荷重を1000kgf としてポンチ３を圧入し、試験片１をコの字型に成形する。試験片１の両面には潤滑剤として防錆油を片面当たり２ｇ／㎡塗布し、ポンチ３の圧入速度は60㎜／分とした。コの字型に成形された試験片の側壁部のビードで押さえられた側の表面に粘着テープを貼り、テープに付着するめっき皮膜の剥離片の状況を目視で判定し、下記の区分で評価した。

【００５２】フレーキング無し：○　　僅かに有り：△
フレーキング有り：×

塗装後鮮映性試験：浸漬式りん酸塩処理を施した鋼板に、カチオン型電着塗料による下塗り20μｍ、中塗り35～40μｍ、上塗り35～40μｍの３コート塗装（合計膜厚：100 μｍ程度）を施した。この試験片の写像鮮明度をＮＳＩＣ値として写像鮮明度測定装置［スガ試験機（株）製ＮＳＩＣ型］を用いて測定し、下記の区分で評価した。なお、ＮＳＩＣ値は、黒板研磨ガラスでは100であり、ＮＳＩＣ値が100 に近いほど良好な鮮映性を示す。

【００５３】

ＮＳＩＣ値　95以上：◎　　94～85：○
80～85：△　　80未満：×

各種の性能評価結果を表２に示す。

【００５４】

【表２】

表2

試番	鋼種	めっき条件 雰囲気露点(℃)	低温保持(秒)	めっき浴Al(重量%)	めっき皮膜構成 化学組成 Al(重量%)	Fe	表面粗さ Ra(μm)	谷ピーク数	性能評価結果 摺動性 摩擦係数(μ)	評価	耐フレーキング性	鮮映性 NSIC値	評価	備考
1	A	−20	40	0.12	0.18	8	0.78	403	0.245	○	○	93	○	
2	A	−30	50	0.13	0.30	10	0.82	521	0.222	◎	○	85	○	本
3	B	−35	50	0.13	0.25	9	0.80	482	0.203	◎	○	88	○	発
4	B	−40	55	0.14	0.38	12	0.92	550	0.191	◎	○	86	○	明
5	B	−30	60	0.12	0.38	12	0.94	550	0.191	◎	○	86	○	例
6	C	−40	40	0.12	0.22	12	0.80	450	0.238	◎	○	96	◎	
7	C	−25	50	0.13	0.35	10	0.85	480	0.212	◎	○	95	◎	
8	C	−20	60	0.14	0.48	10	0.94	585	0.206	◎	○	85	○	
9	D	−30	40	0.12	0.20	12	0.78	420	0.255	○	○	97	◎	
10	D	−40	50	0.13	0.32	9	0.88	498	0.230	◎	○	95	◎	
11	E	−35	40	0.12	0.18	10	0.75	380	0.268	○	○	96	◎	
12	E	−40	50	0.12	0.25	12	0.80	455	0.233	◎	○	98	◎	
13	E	−40	60	0.14	0.50	12	0.93	596	0.210	◎	○	95	◎	
14	F	−40	20	0.12	0.22	9	0.73	320	0.278	○	○	96	◎	
15	F	−40	50	0.13	0.41	10	0.90	510	0.228	◎	○	88	○	
16	G	−35	50	0.13	0.35	13	0.93	538	0.210	◎	○	92	○	
17	H	−30	60	0.14	0.47	9	0.94	585	0.201	◎	○	85	○	
18	I	−20	20	0.12	0.20	11	0.78	350	0.271	○	○	98	◎	
19	I	−25	40	0.13	0.30	15	0.85	452	0.230	◎	○	95	◎	
20	I	−23	60	0.13	0.45	10	0.93	569	0.212	◎	○	95	◎	
21	*J	−40	40	0.13	0.35	10	*1.15	380	0.280	△	△	78	×	
22	*J	−40	*10	0.12	*0.15	10	0.72	*265	0.325	×	×	90	○	比
23	*K	−40	50	0.13	0.40	11	*1.20	398	0.265	○	○	75	×	較
24	*L	−30	50	0.13	0.38	12	*1.08	350	0.285	△	△	80	△	例
25	*M	−40	60	0.13	0.28	9	*1.05	*280	0.320	×	×	83	△	
26	*N	−35	40	0.12	0.20	12	0.90	*310	0.295	△	△	86	○	
27	A	−40	*15	0.14	*0.52	12	*1.12	*680	0.195	◎	○	75	×	
28	B	−40	50	0.12	*0.16	8	0.90	*310	0.296	△	△	98	◎	
29	B	−40	*15	0.12	0.20	10	0.98	*310	0.280	△	△	80	△	

(注) ＊印は本発明の条件を外れるものであることを示す。

【００５５】表２に示されているように母材の化学組成とめっき皮膜構成共に本発明が規定する条件を満たしている試番１～20は耐フレーキング性も塗装後の鮮映性も共に良好である。

【００５６】Si やMn 含有量が本発明が規定する条件を外れている鋼JおよびKを用いた試番21と23は塗装後の鮮映性が劣る。Si 含有量が低く、めっき皮膜中のAl 含有量も本発明が規定する範囲から外れている試番22は、谷ピーク数が本発明の規定する値に満たず耐フレーキング性が好ましくない。Mn が過剰に含有されている試番24、および、Pが過剰に含有されている試番25は、ずれも耐フレーキング性が好ましくない。Ti 含有量が不足した鋼Nを用いた試番26は、鋼中の固溶Cが粒界に偏析して谷ピーク数が不足し耐フレーキング性が好ましくない。

【００５７】試番27は、母材の化学組成は本発明が規定する条件範囲内であるが、めっき皮膜中のAl 含有量が本発明が規定する範囲の上限を超えているために塗装後の鮮映性が劣る。試番28も、母材の化学組成は本発明が＊規定する条件範囲内であるが、めっき皮膜中のAl 含有量が少なすぎるために耐フレーキング性が劣る。試番29は低温保持時の時間が不足したために耐フレーキング性が好ましくない。

【００５８】

【発明の効果】本発明の鋼板はプレス加工時のフレーキング不良が発生し難く、塗装した場合の鮮映性が優れる。これを自動車の外装部品の素材として用いれば、加工工程での歩留まりや作業性が優れ、自動車の外観商品性も優れる。また、この鋼板は本発明が規定する方法によれば、経済的かつ合理的に製造できる。

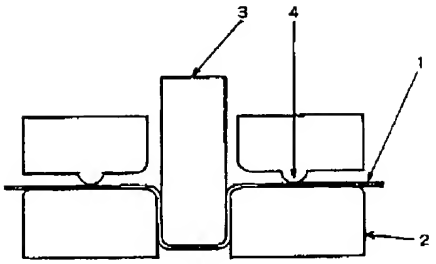
【図面の簡単な説明】

【図１】めっき鋼板の摺動性を評価する装置の断面を示す図である。

【符号の簡単な説明】

１　試験片
２　ダイス
３　ポンチ
４　しわ押さえビード

【図１】



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